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Second day, the precipitate was washed and filtered repeatedly with a total of ~ 12 liter hot DI water (~55-60°C) to a filtrate pH of 6. The washing step included slurring (redispersing) the precipitate into hot water (85-90°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material (color dark brown) was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-021 (1875-B). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

Observations

The final pH (second day, June 29) was ~7, even though more NaOH had been added after the addition of Pt-Ce-Zr solutions.

Results & Analysis

Pt %	Ce %	Ce(III)/Ce(IV)	Zr %	SA, m ² /g	Pore Volume, cc/g	Pore Size Distribution	SBM	TEM	XRD	TPR/TPO	Pulse Chemisorption	ITK	Other

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TITLE

PROJECT NO.

23

BOOK NO.

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File Name: 1875_023 (4%Pt-CeO₂-ZrO₂ 58-42 copp NaOH)

Tested as 1875-C

Catalyst prep: A. Ghenciu/ N. Trusty

5 Objective

WGS Catalyst: Prepare 4%Pt-CeO₂-ZrO₂ (CeO₂:ZrO₂ = 58:42, wt%) by coprecipitation, using nitrate precursors; % metal is by weight.

MATERIALS

(shows actual weights used)

Pt nitrate solution, JM, 233.42 g Pt/l sol, 149.33 g Pt/kg sol, d = 1.5631 g/ml 10.72 g
 Ce(NO₃)₃ stock solution, JM, 395 g Ce/l, d = 1.7 g/ml 78.95 g (~46.5 ml)
 ZrO(NO₃)₂ stock solution, JM, 203 g/l, d = 1.433 g/ml 84.28 g (~58.8 ml)
 NaOH pellets 34.6 g
 Deionized (DI) water (not including the water for washing the precipitate) -2000 ml

Calculation

Calculated for 40 g 4%Pt-CeO₂-ZrO₂ final material, containing:
 38.4 CeO₂-ZrO₂ and 1.6 g Pt

1. Pt nitrate solution needed for 1.6 g Pt:
 $1.6 \times 1000 / 149.33 = 10.715$ g Pt solution (6.855 ml)

2. Ce (III) nitrate solution needed:

for 58% CeO₂, 22.272 g CeO₂ in the final material

moles CeO₂ = $22.272 / 172.12 = 0.129398$ = moles Ce

amount Ce = $0.129398 \times 140.12 = 18.1313$ g

Ce(III) solution = $18.1313 \times 1000 / 395 = 45.90$ ml Ce solution, or $45.90 \times 1.7 = 78.0333$ g Ce solution

3. ZrO²⁺ solution needed:

for 42% ZrO₂, 16.128 g ZrO₂ in the final material

moles ZrO₂ = $16.128 / 123.224 = 0.130884$ = moles Zr

amount Zr = $0.130884 \times 91.224 = 11.9397$ g

ZrO²⁺ solution = $11.9397 \times 1000 / 203 = 58.8164$ ml ZrO²⁺ solution, or $58.8164 \times 1.433 = 84.2839$ g ZrO²⁺ solution

4. NaOH solution needed, 30% excess:

3 moles/ 1 mol Ce (III) solution, 2 moles/ 1 mol ZrO²⁺ solution, 2 moles/ 1 mol Pt solution

$3 \times 0.129398 = 0.388194$ moles NaOH for Ce(III)

$2 \times 0.130884 = 0.261767$ moles NaOH for ZrO²⁺

$2 \times (1.6 / 195.09) = 0.016403$ moles NaOH for Pt

Total moles NaOH = 0.666364 moles; with 30% excess, 0.86627 moles NaOH

NaOH needed: $0.86627 \times 40 = 34.6509$ g

Preparation

The weighed amounts of Pt solution, Ce(III) solution, and zirconyl solution were mixed in an Erlenmeyer flask. The weighed amount of NaOH was brought to a 2-liter solution with DI water, in a volumetric flask (0.43N NaOH solution obtained), then transferred to the reactor.

30 The coprecipitation was conducted at 90-95°C in a 3-liter glass reactor having a heating/cooling mantle, under vigorous stirring, by dosing the Pt - Ce - Zr nitrate solution during ca. 1 hr, subsurface. The pump dial was set at "Other," display 0.5-0.7 in the beginning, then at 2.0, then the dosing accelerated to 3.0 pump dial. During the course of reaction, the color of the precipitate intensified from light yellow to beige, then to brown.

After the addition of the precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C, then washed and filtered repeatedly with a total of ~ 14 liter hot DI water (~55-60°C) to a filtrate pH of 6. The washing step included slurring

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(redispersing) the precipitate into hot water (85-90°C) with stirring, followed by filtration. The conductivity of the filtrate was measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material (color dark brown) was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and 1875-023 (1875-C). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

Observations

Results

Analysis

Pt %	Ce %	Ce(III)/Ce(IV)	Zr %	SA, m ² /g	Pore Volume, cc/g	Pore Size Distribution	SEM	TEM	XRD	TPR/TPO	Pulse Chemisorption	ITK	Other

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PROJECT NO.

BOOK NO.

TITLE

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File Name: 1875_025 (ZrO₂-4%Pt-CeO₂ 42-58 copp NaOH_seq)

Tested as 1875-D

Catalyst prep: A. Ghenciu/ N. Trusty

Objective

WGS Catalyst: Prepare ZrO₂-4%Pt-CeO₂ (CeO₂:ZrO₂ = 58.42, wt%) by sequential coprecipitation, using nitrate precursors; % metal is by weight. Target to obtain Pt-O-Ce(OH)_x, then precipitate Zr(OH)₂.

MATERIALS
(shows actual weights used)

Pt nitrate solution, JM, 233.42 g Pt/l sol, 149.33 g Pt/ kg sol, d = 1.5631 g/ml 8.04 g
 Ce(NO₃)₃ stock solution, JM, 395 g Ce/l, d=1.7 g/ml 59.00 g (~34.7 ml)
 ZrO(NO₃)₂ stock solution, JM, 203 g/l, d = 1.433 g/ml 63.21 g (~44.1 ml)
 NaOH pellets 25.9 g
 Deionized (DI) water (not including the water for washing the precipitate) ~1500 ml

Calculation

Calculated for 30 g 4%Pt-CeO₂-ZrO₂ final material, containing:
 28.8 CeO₂-ZrO₂ and 1.2 g Pt

1. Pt nitrate solution needed for 1.2 g Pt:
 $1.2 \times 1000 / 149.33 = 8.0359$ g Pt solution (5.141 ml)
2. Ce (III) nitrate solution needed:
 for 58% CeO₂, 16.704 g CeO₂ in the final material
 $\text{moles CeO}_2 = 16.704 / 172.12 = 0.09705 = \text{moles Ce}$
 $\text{amount Ce} = 0.09705 \times 140.12 = 13.5984$ g
 $\text{Ce(III) solution} = 13.5984 \times 1000 / 395 = 34.43$ ml Ce solution, or $34.43 \times 1.7 = 58.525$ g Ce solution
3. ZrO₂²⁺ solution needed:
 for 42% ZrO₂, 12.096 g ZrO₂ in the final material
 $\text{moles ZrO}_2 = 12.096 / 123.224 = 0.098163 = \text{moles Zr}$
 $\text{amount Zr} = 0.098163 \times 91.224 = 8.95479$ g
 $\text{ZrO}_2^{2+} \text{ solution} = 8.95479 \times 1000 / 203 = 44.1123$ ml ZrO₂²⁺ solution, or $44.1123 \times 1.433 = 63.213$ g ZrO₂²⁺ solution
4. NaOH solution needed, 30% excess:
 3 moles/ 1 mol Ce (III) solution, 2 moles/ 1 mol ZrO₂²⁺ solution, 2 moles/ 1 mol Pt solution
 $3 \times 0.09705 = 0.29115$ moles NaOH for Ce(III)
 $2 \times 0.098163 = 0.196325$ moles NaOH for ZrO₂²⁺
 $2 \times (1.2 / 195.09) = 0.012302$ moles NaOH for Pt
 $\text{Total moles NaOH} = 0.49977$ moles; with 30% excess, 0.64971 moles NaOH
 $\text{NaOH needed} = 0.64971 \times 40 = 25.9882$ g

Preparation

The weighed amounts of Pt and Ce(III) solutions were stored in an Erlenmeyer flask. The weighed amount of zirconyl solution was stored in another Erlenmeyer flask. The necessary amount of NaOH was brought to 1.5-liter solution with DI water (0.43N NaOH solution obtained), then transferred to the reactor.

The coprecipitation was conducted at 90-95°C in a 1.5-liter glass reactor having a heating/cooling mantle, under vigorous stirring, in the following manner:

- The Pt - Ce nitrate solution was dosed in the NaOH solution during ca. 20 min, subsurface. The pump dial was set at "Other," display 0.5-0.7 in the beginning, then at 2.0 followed by 2.3 pump dial. During the course of the reaction, the color of the precipitate intensified from light yellow to dark beige.
- After the addition of the Pt-Ce solution was complete, the zirconyl solution was added by dosing in the same manner (pump dial 2.5, "Other"). The precipitate became slightly lighter in color, probably due to the formation of Zr(OH)₂.

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After the addition of the Zr precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C, then washed and filtered repeatedly with a total of ~ 11 liter hot DI water (~55-60°C) to a filtrate pH of 6. The washing step included slurring (redispersing) the precipitate in hot water (85-90°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

The material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material (brown color) was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-025 (1875-023). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

Observations:

Compare the performance of 1875-023 and 1875-025 in WGS: Pt-CeO₂ or Pt-Ce-Zr interaction?

Results:

Pt %	Ce %	Ce(III)/Ce(IV)	Zr %	SA, m ² /g	Pore Volume, cc/g	Pore Size Distribution	SEM	TEM	XRD	TPR/TPO	Pulse Chemisorption	ITK	Other

PROJECT NO.

27

BOOK NO.

FILE

File Name: 1875_027 (2%Pt-ZrO₂ copp NaOH)

Tested as 1875-E

Catalyst prep: A. Ghenciu/ N. Trusty

Objective

WGS Catalyst: Prepare 2%Pt-ZrO₂ coprecipitation, using nitrate precursors; % metal is by weight. Target to obtain Pt-O-Zr(OH)_x.

Materials

show actual
weights used

Pt nitrate solution, JM, 233.42 g Pt/l sol, 149.33 g Pt/ kg sol. d = 1.5631 g/ml 5.36 g
ZrO(NO₃)₂ stock solution, JM, 203 g/l, d = 1.433 g/ml 204.9 g (~143 ml)
NaOH pellets 30.9 g
Deionized (DI) water (not including the water for washing the precipitate) ~2000 ml

Calculation

Calculated for 40 g 2%Pt-ZrO₂ final material, containing:
39.2 ZrO₂ and 0.8 g Pt

1. Pt nitrate solution needed for 0.8 g Pt:
 $0.8 * 1000 / 149.33 = 5.3573$ g Pt solution (3.427 ml)

2. ZrO₂⁺ solution needed for 39.2 g ZrO₂ in the final material:
moles ZrO₂ = $39.2 / 123.224 = 0.31807$ = moles Zr
amount Zr = $0.31807 * 91.224 = 29.0155$ g
ZrO₂⁺ solution = $39.0155 * 1000 / 203 = 142.933$ ml ZrO₂⁺ solution, or $142.933 * 1.433 = 204.823$ g ZrO₂⁺ solution

3. NaOH solution needed, 20% excess:
2 moles/ 1 mol ZrO₂⁺ solution, 2 moles/ 1 mol Pt solution
 $2 * 0.31807 = 0.63614$ moles NaOH for ZrO₂⁺
 $2 * (0.8 / 195.09) = 0.008201$ moles NaOH for Pt
Total moles NaOH = 0.64434 moles; with 20% excess, 0.7732 moles NaOH
NaOH needed: $0.7732 * 40 = 30.93$ g

Preparation

The weighed amounts of Pt and zirconyl solutions were stored in an Erlenmeyer flask. The necessary amount of NaOH was brought to 2-liter solution with DI water (0.38N NaOH solution obtained), then transferred to the reactor.

The coprecipitation was conducted at 90-95°C in a 3-liter glass reactor having a heating/cooling mantle, under vigorous stirring, by dosing the Pt - Zr nitrate solution during ca. ½ hr, subsurface. The pump dial was set at "Other," display 0.3-0.8 in the beginning, then at 2.0. During the course of reaction, the color of the precipitate intensified from light yellow to chrome yellow.

After the addition of the Pt-Zr precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C, then washed and filtered repeatedly with a total of ~ 12-13 liter hot DI water (~55-60°C) to a filtrate pH of 6. The washing step included sharring (redispersing) the precipitate in hot water (85-95°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-027 (1875-E). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

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Observations

Results &
Analytical

Pt%	Zr%	SA, m ² /g	Pore Volume, cc/g	Pore Size Distribution	SEM	TEM	XRD	TPR/ TPO	Pulse Chem- isorption	ITK	Other

PROJECT NO.

29

BOOK NO.

TITLE

File Name: 1875_029 (2%Pt-ZrO₂-CeO₂ 42-58 copp NaOH_{seq})

Tested as 1875-F

Catalyst prep: A. Ghenciu/ N. Trusty

Objective

WGS Catalyst: Prepare 2%Pt-ZrO₂-CeO₂ by coprecipitation, using nitrate precursors; % metal is by weight. Target to obtain Pt-O-Zr(OH)_x-Ce(O)_x.MATERIALS
(shows actual
weights used)

Pt nitrate solution, JM, 233.42 g Pt/l sol, 149.33 g Pt/kg sol, d = 1.5631 g/ml 2.68 g
 Ce(NO₃)₃ stock solution, JM, 395 g Ce/l, d=1.7 g/ml 40.0 g (-23.5 ml)
 ZrO(NO₃)₂ stock solution, JM, 203 g/l, d = 1.433 g/ml 43.0 g (-30 ml)
 NaOH pellets 16.1 g
 Deionized (DI) water (not including the water for washing the precipitate) -1000 ml

Calculation

Calculated for 20 g 2%Pt-ZrO-CeO₂ final material, containing:
 19.6 CeO₂-ZrO₂ and 0.4 g Pt

1. Pt nitrate solution needed for 0.4 g Pt:

$$0.4 * 1000 / 149.33 = 2.67863 \text{ g Pt solution (1.714 ml)}$$

2. Ce (III) nitrate solution needed:

for 58% CeO₂, 11.368 g CeO₂ in the final material

$$\text{moles CeO}_2 = 11.368 / 172.12 = 0.066047 = \text{moles Ce}$$

$$\text{amount Ce} = 0.066047 * 140.12 = 9.2545 \text{ g}$$

$$\text{Ce(III) solution} = 9.2545 * 1000 / 395 = 23.43 \text{ ml Ce solution, or } 23.43 * 1.7 = 39.83 \text{ g Ce solution}$$

3. ZrO₂²⁺ solution needed:for 42% ZrO₂, 8.232 g ZrO₂ in the final material

$$\text{moles ZrO}_2 = 8.232 / 123.224 = 0.066805 \text{ moles Zr}$$

$$\text{amount Zr} = 0.066805 * 91.224 = 6.0942 \text{ g}$$

$$\text{ZrO}^{2+} \text{ solution} = 6.0942 * 1000 / 203 = 30.0209 \text{ ml ZrO}^{2+} \text{ solution, or } 30.0209 * 1.433 = 43.02 \text{ g ZrO}^{2+} \text{ solution}$$

4. NaOH solution needed, 20% excess:

3 moles/ 1 mol Ce (III) solution, 2 moles/ 1 mol ZrO₂²⁺ solution, 2 moles/ 1 mol Pt solution

$$3 * 0.066047 = 0.198141 \text{ moles NaOH for Ce(III)}$$

$$2 * 0.066805 = 0.13361 \text{ moles NaOH for ZrO}^{2+}$$

$$2 * (0.4 / 195.09) = 0.0041 \text{ moles NaOH for Pt}$$

$$\text{Total moles NaOH} = 0.33585 \text{ moles; with 20\% excess, } 0.40302 \text{ moles NaOH}$$

$$\text{NaOH needed: } 0.40302 * 40 = 16.12 \text{ g}$$

Preparation:

The weighed amounts of Pt and zirconyl solutions were mixed and stored in an Erlenmeyer flask. The weighed amount of Ce(III) solution was stored in another Erlenmeyer flask. The necessary amount of NaOH was brought to 1-liter solution with DI water (0.4N NaOH solution obtained), then transferred to the reactor.

The coprecipitation was conducted at 90-95°C in a 1.5-liter glass reactor having a heating/cooling mantle, under vigorous stirring, in the following manner:

- The Ce(III) nitrate solution was dosed in the NaOH solution during ca. 20 min. subsurface. The pump dial was set at "Other," display 0.5-0.7 in the beginning, then at 2.0 followed by 2.5 pump dial. During the course of the reaction, the color of the precipitate intensified from light pink-purple to a purple-cocoa color. After the addition of the Ce(III) solution was complete, the precipitate was cured for 1/2 hr at 90-95°C under stirring.

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- The Pt-Zr precursor solution was added by dosing in the same manner, subsurface, ca. 1/2 hr (pump dial 2.0-2.5, "Other"), precipitate turned yellowish-light brown.

The precipitate was cured under stirring for ca. 1 hr at 90°C, then washed and filtered repeatedly with a total of ~ 9-10 liter hot water (~55-60°C) to a filtrate pH of 6. The washing step included slurring (redispersing) the precipitate in hot water (85-95°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-029 (1875-029 F). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

Observations

Physical

Pt %	Ce %	Ce(III)/Ce(IV)	Zr %	SA, m ² /g	Pore Volume, cc/g	Pore Size Distribution	SEM	TEM	XRD	TPR/TPO	Pulse Chemisorption	ITK	Other

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